Palaeogeography, Palaeoclimatology, Palaeoecology 601 (2022) 111102

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

Assessment of pretreatment methods on CIA-K and CALMAG indices and the effects on paleoprecipitation estimates

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ARTICLE INFO

Editor: Howard Falcon-Lang

Keywords:
Paleosols
Paleoclimate reconstruction
Bulk soil geochemistry
Boundary conditions

ABSTRACT

The chemical compositions of paleosols are frequently used to reconstruct paleoclimatic and paleoenvironmental conditions using proxy relationships derived from modern soils. However, through time, some of the proxy relationships have been applied to paleosol types that were not part of the original training data sets, or they have been analyzed following pretreatment steps that were not employed by the original studies without critical evaluation of whether those methodological changes have impacted the interpretation of the data. Here we test pretreatment methods critically using chemical compositions of thirty-two modern soils from California and Texas to evaluate their impact on two of the most commonly employed climofunction indices to estimate mean annual precipitation, CIA-K and CALMAG. Chemical data are generated from paired soils which have underdone two different pretreatment styles, including using weak glacial acetic acid to digest calcite and using no pretreament methods to keep all calcium in the soil, including from pedogenic carbonate. There is little change in major element oxide values from untreated to acid-treated aliquots, except for calcium oxide depletion after pretreatment. In all soils with >2% CaO in the matrix, calcium oxide is significantly depleted by the acid-digestion pretreatment. This acid-digestion pretreatment induces a substantial increase in estimates of mean annual precipitation, which are not in accordance with published meteorological values. The extent to which precipitation estimates are skewed toward higher values as a function of CaO loss is parametrically correlated with calcium carbonate content of the soil material. This has important implications for the appropriate application of CIA-K and CALMAG indices as viable proxies of paleoprecipitation estimates from paleosol profiles that contain pedogenic and/or diagenetic carbonates and we suggest quantitative thresholds for CaO in untreated samples to minimize potential sources of error.

1. Introduction

One method of reconstructing climate in the rock record is the application of physical, mineralogical, and chemical relationships observed between modern soils and their corresponding climates and application of these “climofunctions” to fossil soils, or paleosols. Paleosols are particularly useful climate indicators because they initially form at the nexus of the atmosphere, biosphere, lithosphere, hydrosphere, and cryosphere (i.e., Critical Zones, Ashley, 1998). As a result, paleosols have the potential to record and preserve relevant climate information such as paleo-$p\mathrm{CO}_2$ (e.g., Cerling, 1991; Montañez et al., 2007; Mora et al., 1996; Royer et al., 2004; Yapp and Poths, 1992), paleotemperature (Gallagher and Sheldon, 2013), paleoprecipitation (Nordt and Driese, 2010a; Sheldon et al., 2002; Stinchcomb et al., 2016), and paleohumidity (Gulbranson et al., 2011). Many recent studies have focused on the creation of new proxies that are empirically derived from the bulk geochemistry of modern soils and the application of these proxies to paleosols. Some of these studies are rooted in chemistry and soil science (Rasmussen and Tabor, 2007; Sheldon et al., 2002), and others are based on statistical correlations (Lukens et al., 2019; Lukens et al., 2018; Nordt and Driese, 2010a, 2010b; Stinchcomb et al., 2016) without a process-based mechanistic approach to pedogenesis. No matter what type of chemistry-to-climate correlation is observed in modern soil systems, all of these proxies assume little or no diagenetic

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https://doi.org/10.1016/j.palaeo.2022.111102
Received 17 April 2022; Received in revised form 20 May 2022; Accepted 31 May 2022
Available online 12 June 2022

alteration of the original soil composition. The implications of diagenetic modifications for paleoclimate reconstructions, specifically how the addition of calcite during the lithification process may modify soil chemistry and related weathering index values, remain unexplored. Calcite is one of the most common cements in paleosols (Retallack, 1991), and many of the paleosol-based chemical proxies include calcium concentrations (Lukens et al., 2018; Nordt and Driese, 2010a; Sheldon et al., 2002), so the effects of diagenetic enrichment of calcium associated with carbonate cementation and lithification must be considered. The issue of calcite is important also because it may accumulate in soils through a variety of processes that include evapotranspiration (during pedogenesis) or cementation (during diagenesis). In this regard, the calcium in calcite that is produced through pedogenic processes may be important to include in the transfer functions, while the other diagenetic calcite, including groundwater carbonate that forms in the phreatic zone, will skew the data away from the original pedogenic composition and therefore should be removed if possible.

Both pedogenic and diagenetic processes may have roles in the resulting paleosol carbonate composition, which may contribute calcium to the transfer functions. A literature review shows different pretreatment methods are commonly applied by different research groups before sample analysis and application of bulk soil geochemistry proxies in order to account for these different end members of calcium (e.g., Adams et al., 2011; Alekseeva et al., 2018; Andrews et al., 2017; Beverly et al., 2017; Beverly et al., 2015; Bucher et al., 2020; Delgado et al., 2019; Driese et al., 2018; Driese and Ashley, 2015; Gastaldo et al., 2014; Goldberg and Humayun, 2010; Harper et al., 2021; He et al., 2015; Kraus and Riggins, 2007; Kumaravel et al., 2009; Leary et al., 2017; Kahmann and Driese, 2008; Li et al., 2016, 2022; Lukens et al., 2017; Medaris Jr. et al., 2017; Mouraviev et al., 2020; Myers et al., 2014; Nordt et al., 2015; Pan and Huang, 2014; Prochnow et al., 2006; Rouzaut et al., 2021; Pereira et al., 2015; Sheldon, 2003; Srivastava et al., 2013; Thomas et al., 2011; Varela et al., 2017). Some studies retain all the calcite present in paleosol samples, including both pedogenic and secondary diagenetic cements (e.g., Adams et al., 2011; Beverly et al., 2015; Bucher et al., 2020; Cleveland et al., 2008; Dal'Bó et al., 2010; Delgado et al., 2019; Driese and Ashley, 2015; Driese and Ober, 2005; Harper et al., 2021; Li et al., 2016, 2022; Nordt et al., 2015; Pereira et al., 2015; Rouzaut et al., 2021; Srivastava et al., 2013; Thomas et al., 2011). Other groups conduct an acid dissolution pretreatment in order to remove all of the calcite which could be present in the sample (e.g., Goldberg and Humayun, 2010; Lukens et al., 2017; Mouraviev et al., 2020), remove the calcite through unstated means (Alekseeva et al., 2018), or apply the proxies only to paleosols that lack carbonate (e.g., Hyland and Sheldon, 2013; Sheldon, 2003). Some researchers use a 10% HCl solution (Lukens et al., 2017) or 50% acetic acid solution (Goldberg and Humayun, 2010) to remove carbonate from their samples, while others only analyze samples below a certain weight % CaO (Adams et al., 2011; Kraus and Riggins, 2007; Myers et al., 2014; Prochnow et al., 2006). This diversity of approaches potentially complicates comparisons of paleoprecipitation estimates among various studies because sample selection criteria used to avoid diagenetic effects and chemical pre-treatment protocols are not consistent from one study to the next. These varied approaches reflect concerns related to (1) the empirical nature of the proxies, (2) the lack of cement in modern soils, and (3) the fact that some of these proxies were not designed for, or for which provisos in the original development of the proxy explicitly advise against its application to carbonate-bearing soils and paleosols (Sheldon et al., 2002). This work, along with other recent studies which examine the depth of trenching to remove modern weathering (Kogler and Hembree, 2019), the number of profiles necessary for sampling to resolve outlier results (Dzombak et al., 2021), and the types of analyses and horizons to sample in order to improve error (Hyland and Sheldon, 2016) all serve to refine errors associated with reconstructing paleoclimate from bulk elemental geochemical proxies.

Herein we present results of geochemical analyses from 28 calcareous and 4 non-calcareous modern soil profiles from California and the Gulf-Coast region of Texas, U.S.A, and compare the results of these analyses with measurements of precipitation taken from either the published literature (Texas) or the soil descriptions (California) (Supplemental Table 1) in order to assess how pretreatment methods influence precipitation estimates. The soils, which formed in a range of both environmental and climatic conditions and contain variable amounts of pedogenic calcium carbonate, represent a compositional spectrum that reflects morphologies typical of paleosol profiles prior to diagenetic alteration. Furthermore, the soils from Texas include some of the same series that were used in the creation of the CALMAG transfer function (Nordt and Driese, 2010a). The chemical composition of each of these soils, in terms of major oxide concentrations, is documented without chemical pretreatment ("untreated" samples) and after acid reaction to remove calcite ("acid-treated" samples) to assess the effects of acid treatment on the two most commonly applied chemical weathering indices, CIA-K (for all soils; Sheldon et al., 2002) and CALMAG (for Vertisols; Nordt and Driese, 2010a). Advantages to using modern soil profiles include (1) availability of published measurements of precipitation that may be compared with corresponding MAP estimates calculated from the proxies and (2) lack of chemical modifications associated with deep burial and diagenesis. We can envision a number of other ways in which this could be tested, but because the literature review shows acid dissolution is the most commonly used pretreatment method, we have focused on that approach first. A variety of acids were used by previous researchers, including dilute HCl which is a strong acid, and concentrated (50%) glacial acetic acid. We chose a dilute acid (10% glacial acetic acid) in order to assess how a relatively gentle pretreatment method affects results, given our presumption that harsher acidification methods would have even great impact. This approach allows us to assess both carbonate removal as well as the potential for calcium to be stripped from Ca-saturated phyllosilicates that should otherwise be a part of the proxy relationships.

We demonstrate herein by way of studying modern soil profiles which include calcium ions from both soil-forming calcite and from Ca-saturated phyllosilicates, that acidolysis pretreatment methods have a significant impact on the resulting elemental chemistry of the residual soil materials and strongly bias the resulting proxy estimates of paleoprecipitation from these samples toward higher rainfall values. These estimated results are out of accordance with direct climate measurements, whereas the same untreated samples provide proxy estimates in accordance with published modern mean annual precipitation data. The removal of carbonate, through acidolysis of paleosol matrix material, is most often used to remove calcite cements which are emplaced during diagenesis. However, when acid is added to paleosol matrix, it may remove both calcite and strip base-cation constituents (including Ca^{2+}) away from the phyllosilicate crystal lattices present within the soil matrix, thereby altering not only CaO values but also other major element oxides. These results offer the first insights into how chemical pretreatment methods on bulk paleosol materials, which have undergone diagenetic modification including cementation of the matrix by carbonate, may skew resulting estimates of elemental indices, and the resulting interpretations of paleoprecipitation and paleoclimate which derive from those chemical data. These results enable us to initiate a process of establishing quantitative boundary conditions for the application of elemental index-based paleoprecipitation estimates from paleosols. In constraining these biases, we offer a set of guidelines to inform best practices for application of chemical indices and paleoenvironmental reconstructions from paleosol profiles.

2. Theory of paleoprecipitation proxies

Many paleoenvironmental proxies generated from bulk soil geochemistry are based on the premise that soil weathering is recorded principally by the breakdown of minerals via hydrolysis into recalcitrant clays and chemical leachates (Sheldon et al., 2002; Sheldon and Tabor, 2009). For example, feldspar hydrolysis proceeds as a function of available water, temperature, and acidity to mobilize labile elements (e.g., K^+, Ca^{2+}, Na^+, Mg^{2+}), whereas recalcitrant elements (Al) are retained in clay minerals within the soil (Dzombak and Sheldon, 2020; Nesbitt and Young, 1982; Sheldon et al., 2002). Although K^+ is easily leached, it is also commonly added by metasomatism in the conversion from soil to rock (i.e., *illitization*; Maynard, 1992). Maynard (1992) dealt with this issue by developing the chemical index of alteration minus potassium (CIA—K), which is defined as

$$CIA - K = 100x\frac{Al}{Al + Ca + Na} \tag{1}$$

Using Northern Hemisphere soils cataloged by Marbut (1935), Sheldon et al. (2002) related CIA-K to mean annual precipitation (MAP):

$$Precipitation\left(mm\ yr^{-1}\right) = 221.1e^{0.0197(CIA-K)} \tag{2}$$

with a standard error of ±181 mm per year. Sheldon et al. (2002) proposed that the proxy should work for soils similar to the training dataset, but cautioned against using it for some types of soils, including calcareous soils. Nonetheless, since it was originally proposed, this precipitation proxy has been applied to many different types of paleosols and morphology classes across most of the Phanerozoic and at times, to the Precambrian, including some soil and paleosol types that were advised to specifically exclude from proxy development in that original analysis (Sheldon et al., 2002).

Precipitation proxies have also been developed for specific types of soils (e.g., Sheldon, 2006) and paleosol morphologies in order to address their unique hydrological and weathering conditions. For example, Nordt and Driese (2010a) studied Vertisols, which are incompletely leached soils that persist on the landscapes for extensive periods of time and have evidence of periodic shrink-swell processes (e.g., Ahmad, 1983; Dudal and Eswaran, 1988; Southard et al., 2012; Wilding and Tessier, 1988). While comparatively rare on the modern Earth (~2% of the ice-free land area; Fairbridge and Spaargaren, 2008), these soils have a high potential for preservation in the rock record because of their association with passive margin settings, and therefore have received special attention by geologists and paleoclimatologists. Nordt and Driese (2010a) noted that Ca^{2+} and Mg^{2+} have a stronger correlation with mean annual precipitation than Na^+ because calcium carbonate, detrital clay, and exchangeable Ca^{2+} and Mg^{2+} are more common in Vertisols than in other soil types. The CALMAG weathering index (Nordt and Driese, 2010a) was developed specifically for use with Vertisols and other soils with shrink-swell features using a climosequence in Texas. CALMAG is defined as

$$CALMAG = 100x\frac{Al}{Al + Ca + Mg} \tag{3}$$

The relationship between CALMAG and paleoprecipitation is.

$$\mathrm{MAP}\ \left(\mathrm{mm\ yr^{-1}}\right) = 22.69(\mathrm{CALMAG})–435.8 \tag{4}$$

with a published standard error of ±- 108 mm per year. Importantly, this mathematical relationship cannot be used on Vertisols that occur in climates with less than ~325 mm yr^{-1}, (see Nordt and Driese, 2010a Fig. 3), which is contradicted by the distribution of modern Vertisols and suggests a bias toward overestimation of precipitation in paleosols that initially formed in arid regions.

3. Materials and methods

Soils were selected to represent a range of climates and parent materials, providing a comprehensive suite of soil-forming environments in order to explore which conditions are most affected by pretreatment methodology. The soils from California were collected in the 1960s and 1970s by soil scientists from the USDA-Natural Resources Conservation Service (NRCS) as part of their official soil series descriptions (OSD) and are now archived in the "California Soil Series Pedolarium" at the University of California Department of Land, Air, and Water Resources in Davis, California. The specimens used in this study ($n = 23$; Fig. 1) were sampled from the California Pedolarium by NJT in 1999, subsequently taken to Southern Methodist University (SMU), and are currently stored in the rock and soil collection in the Huffington Department of Earth Sciences. Vertisol samples from Texas in this study ($n = 7$) were collected by Steven G. Driese and Lee Nordt as part of a Vertisol climosequence study (Driese et al., 2005) and are housed at Baylor University (BU; Fig. 1). All of the specimens used in this study were sampled by LAM in 2017, and were completely expended in analysis. However, additional materials are available from the UC Pedolarium and the collections at Baylor University. All samples analyzed here were taken from soil "B" horizons, consistent with standard use of paleosol materials for paleoclimatic reconstructions based upon CIA-K and CALMAG studies (e.g., Sheldon and Tabor, 2009). All of the carbonate in the soils is described in USDA soil descriptions as pedogenic, and therefore while in different stages (sensu Gile, 1961; Machette, 1985), is the result of modern processes and is not relict or inherited. Most of the soils formed on igneous or mudstone parent matieral.

Soil samples were disaggregated using a mortar and pestle and then split into two different aliquots. One aliquot was analyzed without any chemical pre-treatments, and the other aliquot was treated to remove calcite with repeated reactions of 10% glacial acetic acid until no reaction (i.e., effervescence) was observed. Glacial acetic acid was chosen as the digesting medium to remove calcite specifically, as it is less aggressive than other methods (e.g., concentrated or moderately dilute hydrochloric acid) that would not only dissolve the calcite, but also potentially strip calcium from interlayer sites within phyllosilicates, a process sometimes referred to as acid activation (Carroll and Starkey, 1971; see discussion for explanation of acid activation in Čı́čel and Novak, 1977; Ostrom, 1961). While it is unknown how much calcium could be stripped from interlayer phyllosilicates through acidolysis, it is reasonable to assume that the amount is greater than zero. The results presented here are then a *minimum* estimate of the effects that acidolysis pretreatment methods have on the chemical compositions of soil and paleosol materials, and the resulting measured chemical indices and associated proxy estimates of precipitation compared with previous studies which have used concentrated or moderately dilute acids to remove carbonate from paleosol materials. Acidified samples in this study were washed repeatedly with deionized (D.I.) water until the supernatant and D.I. water had the same pH (~5.7), indicating that excess acids had been removed from the paleosol materials; this typically occurred within five separate washes with soil materials, although some samples required as many as eight separate washes. These samples that underwent acidolysis are referred to as "treated" samples. The treated aliquots were then dried, and both treated and untreated samples were ground and mixed as individual samples with lithium metaborate flux before being melted at 1200 °C and fused into glass discs using a Claissee M4. Major element analysis of the discs were determined using a Thermo Scientific ARL Perform'X X-ray Fluorescence (XRF) spectrometer at Southern Methodist University. The XRF is a wavelength dispersive instrument and runs Oxsas and Uniquant software, which were used for calibration. Both in-house standards (PL032) and USGS reference materials are consistently run with unknowns in order to ensure analytical accuracy (see Supplemental Table 3 for reference material values). Replicate analyses of reference materials establish that reproducibility is ±0.16% for major oxides. XRF data are reported in oxide weight-percent values in Supplemental Tables 4 and 5. Approximately one gram of sample was heated in a muffle furnace at 1050 °C for at least one hour, and weight changes to the nearest 0.1 mg were recorded using an analytical balance to determine loss on ignition (LOI). The elemental concentrations for all elemental data are presented as wt%. By convention, the elemental data are converted from oxide weight-percentage to molar ratios through a process of normalization to 100% through generation of a cofactor. These normalized values are also

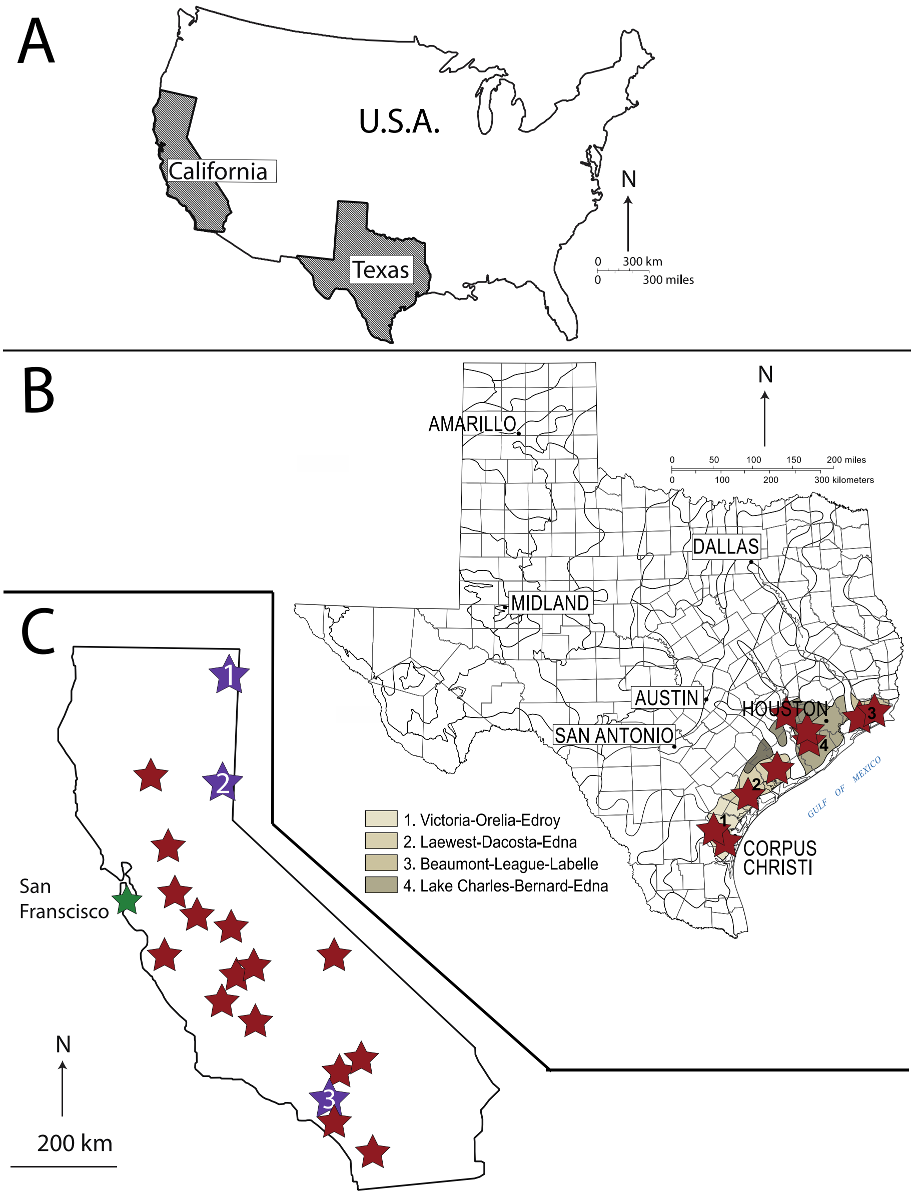

Fig. 1. Soils examined in this study. (A) State political boundaries of California and Texas within the continental United States. (B) Modified Texas soil series map of 2008 with counties outlined, major cities marked, and outlines of soil series mapping units. Stars represent samples that were initially collected for the Vertisol climosequence study of Driese et al. (2005) and were reanalyzed for this study. Latitude and longitude, and UTM, Easting and Northing data for the samples are published in Driese et al. (2005). (C) Locations of soils from California used in this study. Red stars represent the location of soils sampled in the 1960s and 1970s by the USDA-NRCS that are studied here, and the green star denotes the position of the city of San Francisco for reference. Star #1 is the location of three different soils, while stars #2 and #3 represent the site of two different soil sample sites. For GSP coordinates of California sites, see Supplemental Table 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reported in Supplemental Table 5.

4. Results

Because there has been a movement toward soil-specific (and paleosol-specific) taxonomic relationships and their corresponding modern measurements of climate such as precipitation and temperature, the data presented in Supplemental Table 5 are major elemental data acquired through XRF analyses of soil materials, which are binned by USDA soil taxonomic group (Soil Survey Staff, 2010). We acknowledge that major element composition of soils among soil taxonomic groups need not exhibit a parametric correlation, yet this is nevertheless a useful and convenient method to organize and evaluate the resulting data.

When the geochemical data from the untreated and corresponding acid-treated samples are compared, there is an overall increase in CIA-K and CALMAG precipitation estimates for acid treated samples (Fig. 2). The discrepancy between the estimated value and the true value for precipitation increases with increasing removal of CaO through acidolysis.

When the treated versus untreated modern Vertisol samples from Texas ($n = 9$) and California ($n = 1$) are compared, the untreated samples have Al_2O_3 values between 10.56% and 17.84%, and the treated samples have Al_2O_3 values between 11.49% and 17.97% (Fig. 3; Supplemental Table 5). Because Al is the element against which all other elements are compared for both CIA-K and CALMAG, it is worth noting that seven of the Vertisols exhibited increased weight % Al_2O_3 after acid treatment. The CaO values of the untreated Vertisol samples range from 0.68% to 10.13%, whereas the acid-treated samples all have decreased wt% CaO ranging from 0.58% and 4.25% (Fig. 3; Supplemental Table 5). The Na_2O values for the untreated samples range from 0.28% to 2.30%, while the treated samples range from 0.26% to 1.55% (Fig. 3; Supplemental Table 5). MgO values for the untreated Vertisol samples vary between 1.04% and 3.76%, and treated samples range from 1.01% to 4.49% (Fig. 3; Supplemental Table 5).

For the Alfisols from California ($n = 4$), the untreated samples have Al_2O_3 values that range from 15.57% to 17.18%, and the acid-treated samples range between 15.52% and 17.37% (Fig. 3; Supplemental Table 5). The CaO values of the untreated samples are between 2.04% and 3.15%, while the acid-treated samples are between 1.62% and

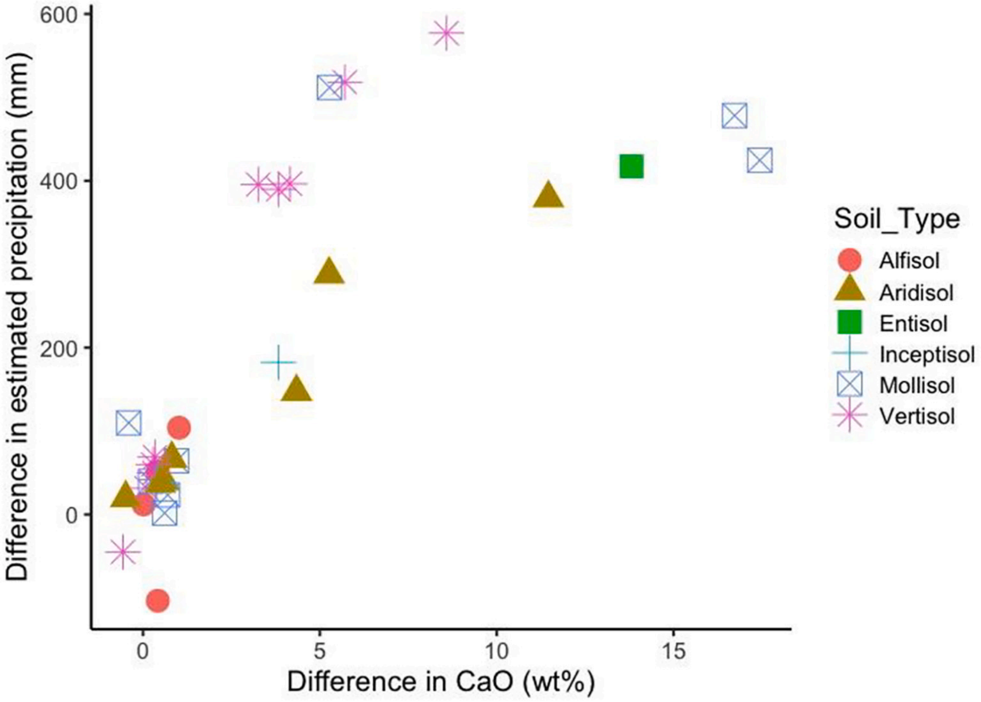

Fig. 2. Difference in precipitation calculations based on treatment methods plotted versus the difference in the weight percent CaO normalized to 100%. Vertisols (pink stars) are from Texas and California while Alfisols (pink circle), Mollisols (blue x in box), Aridisols (brown triangle), Entisols (green square), and Inceptisols (light blue plus sign) were all collected in California. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

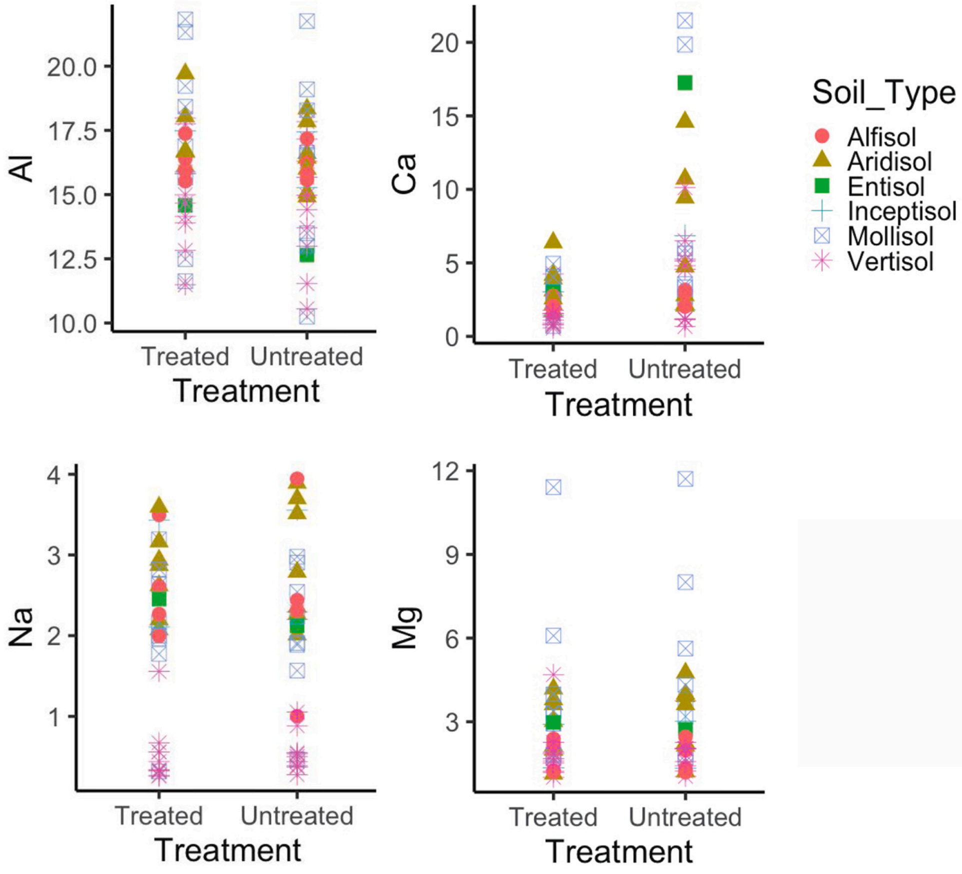

Fig. 3. Bulk soil elemental oxides data for elements in the CIA-K and CALMAG equations versus treatment methods for soils studied here. See Supplemental Table 5 for elemental oxide data.

2.96%. The Na_2O values of untreated samples range from 1.00% to 3.95%, while the acid-treated samples range from 2.00% to 3.50%. The untreated samples have MgO values between 1.19% and 3.46%, while the acid-treated samples range from 1.20% to 2.39%.

For the Aridisols from California ($n = 7$), the untreated samples have Al_2O_3 values that range from 14.92% to 18.34%, and the acid-treated samples range from 16.10% to 19.71% (Fig. 3; Supplemental Table 5). The untreated CaO values range from 2.08% to 14.59%, while the acid-treated samples range from 1.72% to 6.39%. Na_2O values of untreated samples range from 2.27% to 3.89%, and acid-treated samples range from 2.01% to 3.70%. The MgO weight percent of untreated samples is between 1.21% and 4.75%, while acid-treated samples range from 1.13% to 4.18%.

For the Mollisols from California ($n = 8$), the untreated samples have Al_2O_3 values between 10.25% and 21.75%, and acid-treated values between 11.63% and 21.82% (Fig. 3; Supplemental Table 5). Of these eight samples, seven exhibit increased aluminum values following acid digestion. The CaO weight % of untreated samples is 2.63% to 16.38%, while acid-treated samples vary between 0.61% and 4.42%. Untreated samples have Na_2O values that vary between 0.47% and 2.98%, while acid-treated samples vary between 0.32% and 3.19%. MgO values of untreated samples are between 1.69% and 11.71%, and acid-treated samples range from 1.71% to 11.41%.

The Entisol ($n = 1$) from California has Al_2O_3 values of 12.62% (untreated) and 14.58% (acid-treated), CaO values of 17.26% (untreated) and 3.45% (acid-treated), Na_2O values of 2.12% (untreated) and 2.45% (acid-treated), and MgO values of 2.72% (untreated) and 2.98% (acid-treated) (Fig. 3; Supplemental Table 5). The untreated Inceptisols from California ($n = 2$) have Al_2O_3 values of 15.27% and 17.44%, and acid-treated samples have values of 15.83% and 17.48%. The untreated samples have CaO values of 6.86% and 1.80%, and the treated samples are 3.03% and 1.41%. Na_2O values for untreated samples are 3.55% and 2.20%, and acid-treated samples are 3.42% and 2.11%. MgO values for untreated samples are 2.57% and 1.32%, while acid-treated samples are 2.70% and 1.25%.

Alfisols have the smallest difference in weight % CaO between pretreatment methods (0.02% to 1.02%) (Figs. 2, 3). Inceptisols have a difference in weight % CaO of 0.39% to 3.83%. Vertisols have a difference in weight % CaO between −0.57% and 8.58%. Aridisols' weight % CaO varies between −0.49% and 11.46%, while the only Entisol has a difference in weight % CaO of 13.81%. Mollisols have the largest difference in weight % CaO between pretreatment methods (−0.41 to 17.43%) (Supplemental Table 5). There is a statistically significant difference in the group average of normalized weight % CaO between the treated and untreated soils ($p = 0.0015225$).

Weight percent oxide values of Alfisols correspond to CIA-K precipitation estimates between 890 mm yr^{-1} and 1160 mm yr^{-1} (Supplemental Table 6). Estimates for untreated samples vary between 890 mm yr^{-1} to 1160 mm yr^{-1} and treated samples vary from 943 mm yr^{-1} to 1060 mm yr^{-1}. Aridisols have geochemical values that correspond to CIA-K precipitation estimates between 560 mm yr^{-1} to 1100 mm yr^{-1}. Untreated samples vary from 560 mm yr^{-1} to 1063 mm yr^{-1}, and acid-treated samples vary between 781 mm yr^{-1} and 1100 mm yr^{-1}. The Entisol geochemical values correspond to CIA-K precipitation estimates of 480 mm yr^{-1} for the untreated aliquot, whereas the acid-treated aliquot corresponds to 900 mm yr^{-1}. Inceptisols have geochemical values that correspond to CIA-K precipitation estimates ranging from 713 mm yr^{-1} to 1100 mm yr^{-1}, whereas acid-treated Inceptisols have CIA-K estimates that range from 895 mm yr^{-1} to 1140 mm yr^{-1}. Mollisols have geochemical values that correspond to CIA-K precipitation estimates ranging from 415 mm yr^{-1} to 1350 mm yr^{-1}. Untreated samples have CIA-K precipitation estimates which range between 415 mm yr^{-1} to 1090 mm yr^{-1}, whereas acid-treated samples range from 838 mm yr^{-1} to 1350 mm yr^{-1}. Vertisols have geochemical compositions which correspond to CIA-K precipitation estimates between 575 mm yr^{-1} to 1412 mm yr^{-1}. Untreated samples have chemical compositions which correspond to CIA-K precipitation estimates that vary from 575 mm yr^{-1} to 1339 mm yr^{-1}, whereas acid-treated samples vary from 934 mm yr^{-1} to 1412 mm yr^{-1}. Geochemical compositions of Vertisols analyzed in this study correspond to CALMAG precipitation estimates which range from 640 mm yr^{-1} to 1596 mm yr^{-1}. Untreated samples range from 640 mm yr^{-1} to 1553 mm yr^{-1}, whereas acid-treated samples range from 1013 mm yr^{-1} to 1596 mm yr^{-1}.

Mollisols record a difference in geochemical compositions based on pretreatment methods that corresponds to a difference in CIA-K precipitation estimates ranging from 1 mm yr^{-1} to 512 mm yr^{-1} ($n = 8$; Fig. 2; Supplemental Table 6). Alfisols record a difference in geochemical compositions based on pretreatment methods that corresponds to a difference in CIA-K precipitation estimates ranging from 12 mm yr^{-1} to 104 mm yr^{-1} ($n = 4$), while Aridisols vary between 19 mm yr^{-1} to 379 mm yr^{-1} ($n = 7$) (Fig. 2; Supplemental Table 6). Depending on the proxy applied, Vertisols ($n = 10$) record a difference in geochemical compositions based on pretreatment methods that corresponds to a difference in CIA-K precipitation estimates ranging from 31 mm yr^{-1} to 577 mm yr^{-1} and a difference in CALMAG precipitation estimates ranging from 37 mm yr^{-1} to 714 mm yr^{-1} (Fig. 2; Supplemental Table 6), which on average exceeds the stated error of the proxy.

Although it has been suggested that Entisols and some Inceptisols should not be used for paleoclimate reconstruction because they are not in equilibrium with their environments (e.g., Sheldon et al., 2002), this study nonetheless includes samples of these soil orders to evaluate the impact of pretreatment methods. Based on pretreatment methods, the Entisol ($n = 1$) records a difference in geochemical compositions that corresponds to CIA-K precipitation estimates ranging from 418 mm yr^{-1}, whereas the Inceptisols ($n = 2$) record differences in geochemical compositions that correspond to differences in CIA-K precipitation estimates ranging from 42 mm yr^{-1} to 183 mm yr^{-1}. While one does not want to over-interpret small datasets, it is notable that the discrepancies between untreated and acid-treated sample pairs is at or larger than the stated error of the proxy in the original work (Sheldon et al., 2002).

5. Discussion

5.1. Problems with paleosol-based paleoclimate proxies

Because paleosols are a common stratigraphic component of continental and mixed-marine-continental successions, the paleoclimate proxies that can be applied to these paleosols using bulk geochemical data are potentially powerful tools with wide-ranging utility. However, these types of paleoclimate reconstructions have become so ubiquitous that many researchers approach their use in a 'blackbox' manner, plugging data gathered from an ICP-MS/IC-AES or XRF into now well-known formulas for precipitation estimates without consideration of pedogenic and diagenetic processes as well as uncertainties of methodological and analytical effects for resulting measurements. While these proxies are easy to use and have a low standard error reported for associated precipitation estimates, their application requires a robust understanding of the soils and boundary conditions used to develop the models and a thoughtful consideration of pretreatment methodology. If these precipitation proxies are applied indiscriminately it is possible that they will generate unreliable results. As a result, it is imperative that researchers understand the soils that went into the creation of the proxy-data training sets as well as appropriate methodology for pretreatment and correction of the data, and to use mechanistic models that are rooted in science, not solely on statistical correlation, before any proxy is used in a study. Sheldon et al. (2002) initially published the soil data and descriptions cataloged by Marbut (1935) and the corresponding climate data together as supplemental materials in the *Journal of Geology*. However, we note that in the digitization of the article, the original data tables were not included. Although it is beyond the scope of this paper to rectify that issue, this author group will redeposit that full dataset into an open access archive to ensure that future workers may interrogate the foundational data.

The original paper describing the CIA-K climofunction (Sheldon et al., 2002) advocated for avoiding carbonate-bearing paleosols rather than chemically removing calcite. Nevertheless, a number of studies have applied the CIA-K proxy to acid-treated carbonate-bearing samples without accounting for the difference in methodology (e.g., Lukens et al., 2017; Mouraviev et al., 2020). The application of this proxy to inappropriate carbonate-bearing paleosols means that the published error does not take into consideration biases in pretreatment methodology published here. In most cases, the published error of 182 mm yr^{-1} for CIA-K does not fundamentally affect reconstruction of paleo-biomes from paleosol data. However, the difference in MAP calculations with pretreatment methods can be as large as 577 mm yr^{-1} for CIA-K and up to 715 mm yr^{-1} for CALMAG (see Fig. 2), and would lead to erroneous reconstruction of paleo-biomes from the same paleosol data, due to methodological protocols which induce irreversible chemical changes to the samples. These pretreatment errors are in excess of the published errors associated with the regressions derived from the datasets used to generate the proxies. The upper limit of this pretreatment error range for the CIA-K proxy means that paleosols formed in a cold desert could appear to reflect development in a boreal forest, or vice-versa. Similarly, soils formed in a warm desert could be interpreted as evidence of a woodland environment, or vice versa. This error has the same implications for biome reconstructions from paleo-Vertisols using the CALMAG proxy. As noted previously by Myers et al. (2014), removal of diagenetic calcite cement to improve the accuracy of paleoprecipitation estimates also removes any detrital or pedogenic calcite, creating a bias toward erroneously high precipitation estimates. It is worth noting that not all of the biases imparted by these pretreatment methods are the same, which is an important consideration for scientists when selecting a paleoprecipitation index. Vertisols, Mollisols, and Aridisols have a larger difference in estimated precipitation with the different pretreatment methods employed, while Alfisols have a smaller difference in precipitation estimates. Future work may consider more soil-specific precipitation estimates for paleoprecipitation given the difference in clay mineralogy found between difference soil series. For example, Sheldon et al. (2002) initially proposed a Mollisol-specific precipitation equation which may be more appropriate for these soils give the likelihood of carbonate in this soil type.

5.2. Toward a mechanistic understanding of the pretreatment bias

There is an additional potential bias imparted when calcite is digested and leached away from paleosol matrix materials with a sufficiently strong acid (e.g., Bauer and Berger, 1998; Carroll and Starkey, 1971). Strong inorganic acids react with and modify the clay structure through a process known as “acid dissolution” or “acid activation”. Excess H^+ that is not involved in calcite digestion causes protonation of the clay layers, stripping exchangeable cations out of the tetrahedral-octahedral-tetrahedral structures of 2:1 exchangeable phyllosilicates and replacing them with H^+ ions, before attacking the layers themselves (Bendou and Amrani, 2014; Čí̌cel and Komadel, 1994; Komadel, 2016; Pentrák et al., 2012). The specific elements removed via acid activation will depend on the phyllosilicates present in the sample, the elemental chemistry of those clays, the acid type and concentration, the ratio of sample to acid, the temperature, and the time the acid interacts with the phyllosilicates. These elements may include removal of Ca^{2+} ions, ferric and ferrous iron, aluminum, and magnesium in bentonites (Komadel, 2016; Komadel and Madejová, 2006). Samples with higher concentrations of Mg^{2+} and/or Fe^{3+} in the octahedral sheets may be removed from the structure more readily than Al (Breen et al., 1995; Čí̌cel and Novak, 1977; Komadel et al., 1996; Novák and Čí̌cel, 1978; Osthaus, 1955; Pentrák et al., 2012). Given the role that these ions play in the precipitation proxies, MAP estimates based on aggressive-acid-treated samples should be treated with caution and assumed to be biased toward higher paleoprecipitation estimates than were actually experienced during soil formation, or pedogenesis (see discussion below). Weak-acid treatments such as acid fumigation as applied in stable isotope soil studies (e.g., Ramnarine et al., 2011) may remove carbonate without changing the clay elemental composition, but Ca^{2+} from $CaCO_3$ breakdown will be retained with the sample as a $CaCl_2$ or some similar reaction derivative. We are unaware of any attempts to employ that fumigation approach for elemental chemistry. Nevertheless, considering the retention of $CaCl_2$ with the reaction products, it seems likely this method will have its own problems of quantitative analysis. Future work may look at additional and different pretreatment methods, including acid fumigation versus decanting to study biases imparted based on these different methods.

Precipitation measurements for the California soils were collected from USDA soil series descriptions which can be accessed through the USDA portal (https://soilseries.sc.egov.usda.gov/osdname.aspx). For soils that form over a reported range of precipitation measurements, an average was taken. The precipitation estimates for the Texas soils were taken from values published in the literature (Nordt and Driese, 2010b). The historical precipitation measurements that are associated with the modern soils analyzed herein, show a more robust correlation with precipitation estimates from untreated samples (Fig. 4). This is true for the majority of both the CIA-K (Fig. 4A) and CALMAG (Fig. 4B) proxies, wherein the values of untreated samples plot closer to the 1:1 line representing comparisons of measured versus estimated rainfall (Fig. 4). Furthermore, it appears that the CIA-K proxy does a slightly better job of estimating precipitation for Vertisols than the CALMAG proxy (Fig. 4C). Acid-treated samples consistently yield higher MAP estimates using both the CIA-K and CALMAG proxies regardless of soil type and fall further off the 1:1 line (Fig. 4C). However, CALMAG seems to consistently overestimate precipitation relative to the CIA-K index (Fig. 4C), and as such Vertisols which undergo acid treatment seem to overestimate precipitation to an even greater amount than CIA-K (Fig. 4C).

In light of the results presented here, previously published precipitation estimates derived from geochemical proxies that used calcareous paleosols are suspect and might, at best, be regarded as equivocal paleoprecipitation estimates. While previous studies have emphasized that CIA-K should not be applied to paleosols with subsurface carbonate (Sheldon and Tabor, 2009), because of excess Ca^{2+}-salts accumulated in the profile, this study demonstrates that calcareous paleosols do not offer reliable proxies of paleoprecipitation for any of the published proxies. There is a relationship between the difference in the weight percent CaO (the contribution of weight percent CaO as a result of calcite vs clay/feldspar) and the difference in precipitation estimates generated by the different proxies (Figs. 1, 4). Given that there are larger errors associated with greater amounts of CaO derived from calcite, we suggest not applying bulk geochemical proxies to any paleosol that has a difference in weight percent CaO $>2\%$ between untreated and acid-treated samples (Fig. 5). For paleosols that have a weight % CaO $<2\%$, paleoprecipitation estimates should be calculated using untreated samples, and a larger error should be assessed to those paleoprecipitation values than those previously reported in the literature. Geochemical results of these untreated samples should be regarded as providing minimum mean annual precipitation estimates. For samples that have only calcite cement, samples should be treated with a weak acid, and geochemical results should be regarded as maximum mean annual precipitation estimates, and a larger error should be assessed than previously reported.

At the other end of potential CaO compositional space, Dzombak et al. (2021) have also recently proposed thresholds for suspecting secondary calcite addition in paleosols using a dataset of >4800 A and C horizons, and $n = 241$ B horizons. They found that for most soil orders, untreated B-horizon values >17% CaO or A horizon values >8.5% CaO (i.e., 95% confidence interval) would likely reflect secondary calcite addition. Using the criteria of Dzombak et al. (2021) herein, all but one of the untreated samples would be considered potentially analyzable for paleoclimatic purposes. However, the thresholds for individual soil orders would be different as virtually all of the higher B horizon CaO

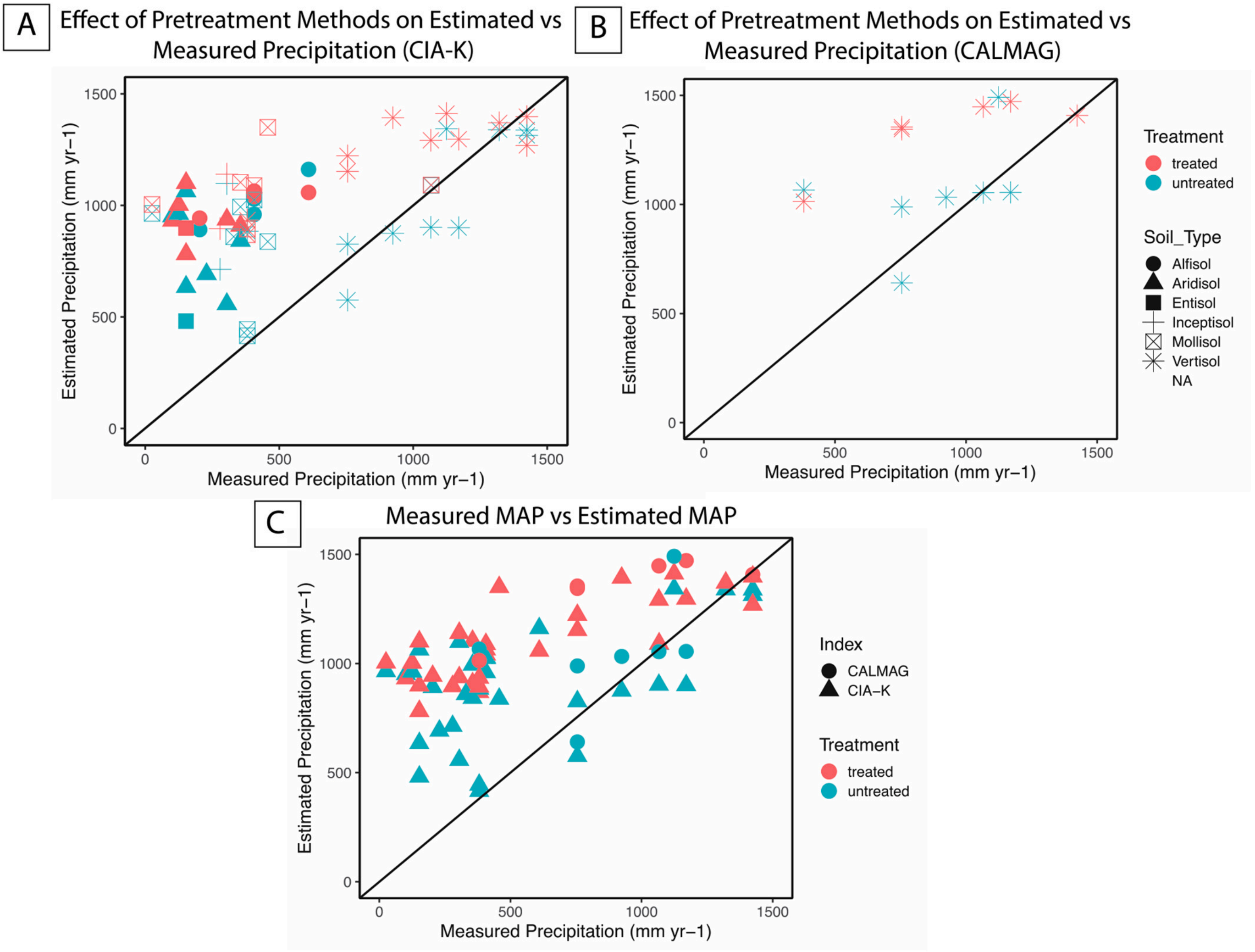

Fig. 4. Precipitation values estimated using the (A) CIA-K or (B) CALMAG proxy compared to the actual historical precipitation measured from meteorological stations near the modern soils from California and Texas. Precipitation values were collected from USDA soil series descriptions. Precipitation values for Texas soils were published in Driese et al. (2005). Line represents a 1:1 line for reference. See text for discussion. (C) Comparison of CIA-K and CALMAG proxies to modern measured values.

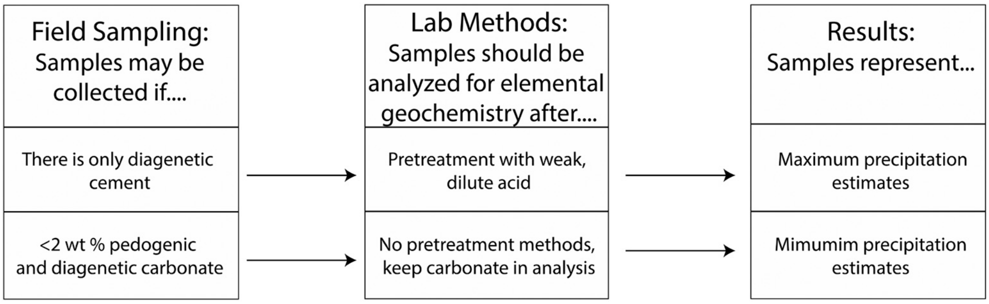

Fig. 5. Guidelines for collection of paleosols that have pedogenic carbonate and/or calcite cement, laboratory pretreatment, and suggestions for interpretations of results.

values come either from Mollisols or Aridisols. For Vertisols or Inceptisols, the threshold is <10%. So conservatively, we would suggest that paleosols with CaO < 2% are likely to produce the most accurate results, those with 2% < CaO < 10% could produce potentially reasonable paleoclimatic results (if the untreated and treated CaO measurements were within 2% of one another), and that paleosols with untreated CaO values >10% should be avoided for any type of chemical-index based precipitation estimate.

Other types of diagenesis may similarly bias paleoprecipitation reconstructions. While the results in this study cannot be used to assign additional error precisely to paleoprecipitation estimates because the chemical effects of acid pretreatment to materials that have undergone burial and diagenesis are not fully evaluated, they nonetheless suggest the potential for systematic biases toward higher mean annual precipitation estimates from geochemical data, particularly for the CALMAG proxy (Fig. 4) when acidolysis-pretreatment methods are involved. For example, phyllosilicates in the clay-sized fractions of mudrocks that typically preserve paleosols frequently undergo chemical and mineralogical transformations as a result of burial diagenesis. In particular, the process of diagenetic illitization removes original cations such as Ca^{2+} and Na^{+}, which reside in the interlayers of 2:1 phyllosilicates and replaces them with K^{+} or NH^{4+} cations. The addition of K^{+} and NH_4^{+} during diagenesis is well documented by X-ray studies, as well as K—Ar dating of phyllosilicates (Clauer et al., 2010; Drits et al., 1997; Elliott and Matisoff, 1996). Note that K^{+} ions are not part of either the CIA-K or CALMAG proxies, and NH_4^{+} ions are not even measured by standard XRF or ICP-OES measurements. Yet, disregarding the composition of K^{+} and NH_4^{+} in paleosols that have undergone diagenesis and potentially undergone illitization virtually ensures the CIA-K and CALMAG values are higher than they were during pedogenesis, which would lead to over-estimates of paleoprecipitation. Future studies will need to focus on the process of chemical diagenesis in paleosol materials to evaluate whether systematic changes occur in the diagenetic alteration of these materials and determine the true error of the CIA-K and CALMAG proxies. The data presented here highlight the need for the community to make a collective effort to reassess the controls and variables that are responsible for bulk elemental data values collected from soils and paleosols.

6. Conclusions

A total of 32 modern soil profiles from Texas and California which span a range of environments and climates have been subjected to different chemical pretreatment methods in order to evaluate whether these methods impart chemical biases which result in equivocal estimates of precipitation compared with recorded measurement near the sample sites. It is likely that acidolysis results in the complete removal of all carbonate minerals as well as Ca^{2+} that resides in the interlayers of some soil phyllosilicates. This causes a statistically significant difference in the CaO weight % values between those samples which underwent acidolysis (treated) compared with those which have had no pretreatment methods applied to them (untreated). This removal of cation by mass action causes a measurable difference in overall weight % oxide values, which imparts a bias on estimates of precipitation which are not in accordance with published measurements by a factor consistent with the difference in CaO content in the treated versus untreated samples. As a result of the deviation of precipitation estimates of acid-treated samples from the same estimates of untreated samples which conform with recorded weather data, we reaffirm previous suggestions to avoid using these paleoprecipitation proxies in paleosol samples with >2 wt% CaO. In practice, this could eliminate essentially all profiles which have seen a substantial diagenetic history that includes carbonate cementation. Future work should focus on evaluating such diagenetically altered paleosol profiles.

In addition, as demonstrated herein, there is an evident need to clearly define what are the boundary conditions that define the limitations of the bulk elemental geochemistry proxies, and which samples are most appropriate for application of paleoprecipitation proxies. As shown here, methodologies might include not only sample collection protocols, but what, if any, pretreatments have been applied to those samples, and a salient evaluation of how those pretreatments may affect the resulting measurements of chemical indices and the resulting estimates of paleoprecipitation. These points cannot be overstated if the community's goal is to work toward quantitative estimates of paleoclimate.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors wish to thank Steven Driese for access to samples from the Texas climosequence. The authors wish to thank Amanda Carroll for the insightful conversations about acid activation, and Crayton Yapp for discussions about the importance of understanding boundary conditions. The authors wish to thank Editor-in-Chief Algeo, Managing Editor Basilici, and Erik Gulbranson and two ananomous reviewers for their constructive feedback. This work has been generously funded by Tennessee Tech University to LAM and Southern Methodist University to NJT and TSM. NJT would like to acknowledge funding through NSF grants EAR-IES-1714797, EAR 1734608, OPP 1341376, and EAR-0844147. NDS would like to acknowledge funding through NSF Grant EAR-1812949.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.palaeo.2022.111102.

References

Adams, J.S., Kraus, M.J., Wing, S.L., 2011. Evaluating the use of weathering indices for determining mean annual precipitation in the ancient statigraphic record. Palaeogeogr. Palaeoclimatol. Palaeoecol. 309, 358–366.

Ahmad, N., 1983. Vertisols. In: Wilding, L.P., Smeck, N.E., Hall, G.F. (Eds.), Pedogenesis and Soil Taxonomy. II. The Soil Orders. Elsevier, New York, pp. 9–123.

Alekseeva, T.V., Alekseev, A.O., Kalinin, P.I., 2018. The Mississippian Paleosols in the Brontsy Quarry, Kaluga region. Earasian Soil Sci. 51, 744–757.

Andrews, E., White, T., del Papa, C., 2017. Paleosol-Based Paleoclimate Reconstruction of the Paleocene Eocene Thermal Maximum, Northern Argentina. Palaeogeogr. Palaeoclimatol. Palaeoecol. 471.

Ashley, G.M., 1998. Where are we headed? "Soft" rock research into the new millennium. In: Geological Society of America Abstracts with Programs (p. A-148).

Bauer, A., Berger, G., 1998. Kaolinite and smectite dissolution rate in high molar KOH solutions at 35° and 80°C. Appl. Geochem. 13, 905–916. https://doi.org/10.1016/S0883-2927(98)00018-3.

Bendou, S., Amrani, M., 2014. Effect of Hydrochloric Acid on the Structural of Sodic-Bentonite Clay. J. Miner. Mater. Charact. Eng. 2, 404–413.

Beverly, E.J., Driese, S.G., Peppe, D.J., Arellano, L.N., Blegen, N., Faith, J.T., Tryon, C.A., 2015. Reconstruction of a semi-arid late Pleistocene paleocatena from the Lake Victoria region, Kenya. Quat. Res. 84, 368–381.

Beverly, E.J., Peppe, D.J., Driese, S.G., Blegen, N., Faith, J.T., Tyron, C.A., Stinchcomb, G.E., 2017. Reconstruction of late Pleistocene Paleoenvironments using Bulk Geochemistry of Paleosols from the Lake Victoria Region. Front. Earth Sci. 5, 93. https://doi.org/10.3389/feart.2017.00093.

Breen, C., Madejová, J., Komadel, P., 1995. Correlation of catalytic activity with infrared, 29Si MAS NMR and acidity data for HCl-treated fine fractions of montmorillonites. Appl. Clay Sci. 10, 219–230. https://doi.org/10.1016/0169-1317(95)00024-X.

Bucher, J., Varela, A., D'Elia, L., Bilmes, A., López, M., García, M., Franzese, J., 2020. Multiproxy paleosol evidence for a rain shadow effect linked to Miocene uplift of the North Patagonian Andes. GSA Bull. 132, 1603–1614.

Carroll, D., Starkey, H.C., 1971. Reactivity of Clay Minerals with Acids and Alkalies. Clay Clay Miner. 19, 321–333.

Cerling, T.E., 1991. Carbon Dioxide in the Atmosphere: evidence from Cenozoic and Mesozoic Paleosols. Am. J. Sci. 291, 377–400.

Čı́čel, B., Komadel, P., 1994. Structural Formulae of Layer Silicates. Quant. Methods Soil Mineral., ASA, CSSA, and SSSA Books. https://doi.org/10.2136/1994.quantitativemethods.c4.

Čı́čel, B., Novak, I., 1977. Dissolution of smectites in hydrochloric acid. I. Half-time of dissolution as a measure of reaction rate. In: Konta, J. (Ed.), Proceedings 7th Conference Clay Minearl Petrology. Charles University, Karlovy Vary, Prague, pp. 163–175.

Clauer, N., Liewig, N., Bobos, I., 2010. K-Ar, δ18O and REE constraints on the genesis of ammonium illite from the Harghita Băi hydrothermal system, Romania. Clay Miner. 45, 393–411. https://doi.org/10.1180/claymin.2010.045.3.393.

Cleveland, D.M., Nordt, L.C., Dworkin, S.I., Atchley, S.C., 2008. Pedogenic carbonate isotopes as evidence for extreme climatic events preceding the Triassic-Jurassic boundary: Implications for the biotic crisis? GSA Bull. 120, 1408–1415.

Dal'Bó, P.F.F., Basilici, G., Angélica Rômulo, S., 2010. Factors of paleosol formation in a late cretaceous eolian sand sheet paleoenvironment, Marília Formation, Southeastern Brazil. Palaeogeogr. Palaeoclimatol. Palaeoecol. 292, 349–365.

Delgado, L., Batezelli, A., Ladeira, F.S.B., Luna, J., 2019. Paleoenvironmental and paleoclimatic interpretation of the late cretaceous Marília Formation (Brazil) based on paleosol geochemistry. Catena 180, 365–382.

Driese, S.G., Ashley, G.M., 2015. Paleoenvironmental reconstruction of a paleosol catena, the Zinj archeological level, Olduvai Gorge, Tanzania. Quat. Res. 85, 133–146.

Driese, S.G., Ober, E.G., 2005. Paleopedologic and Paleohydrologic Records of Precipitation Seasonality from early Pennsylvanian "Underclay" Paleosols, U.S.a. J. Sediment. Res. 75, 997–1010.

Driese, S.G., Nordt, L.C., Lynn, W.C., Stiles, C.A., Mora, C.I., Wilding, L.P., 2005. Distinguishing climate in the Soil Record using Chemical Trends in a Vertisol Climosequence from the Texas Coast Prairie, and Application to Interpreting Paleozoic Paleosols in the Appalachian Basin, U.S.a. J. Sediment. Res. 75, 339–349.

Driese, S.G., Medaris Jr., L.G., Kirsimäe, K., Somelar, P., Stinchcomb, G.E., 2018. Oxisolic processes and geochemical constraints on duration of weathering for Neoproterozoic Baltic paleosols. Precambrian Res. 310, 165–178.

Drits, V.A., Lindgreen, H., Salyn, A.L., 1997. Determination of the content and distribution of fixed ammonium in illite-smecite by X-ray diffraction: Application to North Sea illite-smectite. Am. Mineral. 82, 79–87.

Dudal, R., Eswaran, H., 1988. Distrubution, properties adn classification of Vertisols. In: Wilding, L.P., Puentes, R. (Eds.), Vertisols: Their Distribution, Properties, Classification and Management. Texas A&M University Printing Center, College Station, Texas, pp. 1–22.

Dzombak, R.M., Sheldon, N.D., 2020. Weathering intensity and presence of vegetation are key controls on soil phosphorus concentrations: implications for past and futrue terrestrial ecosystems. Soil Syst. 4, 73. https://doi.org/10.3390/soilsystems4040073.

Dzombak, R.M., Midttun, N.C., Stein, R.A., 2021. Incorporating lateral variability and extent of paleosols into proxy uncertainty. Palaeogeogr. Palaeoclimatol. Palaeoecol. 582 https://doi.org/10.1016/j.palaeo.2021.110641.

Elliott, C., Matisoff, G., 1996. Evaluation of Kinetic Models from the Smectite to Illite Transformation. Clay Clay Miner. 44, 77–87.

Fairbridge, R.W., Spaargaren, O., 2008. Vertisols. In: Chesworth, W. (Ed.), Encyclopedia of Soil Science. Springer, Dordrecht.

Gallagher, T.M., Sheldon, N.D., 2013. A new paleothermometer for forest paleosols and its implications for Cenozoic climate. Geology 41, 647–650.

Gastaldo, R.A., Knight, C.L., Neveling, J., Tabor, N.J., 2014. Latest Permian paleosols from Wapadsberg Pass, South Africa: Implications for Changhsingian climate. GSA Bull. 126, 665–679.

Gile, L.H., 1961. A Classification of ca Horizons in Soils of a Desert Region, Dona Ana County, New Mexico. Soil Sci. Soc. Am. Proc. 25, 52–61.

Goldberg, K., Humayun, M., 2010. The application of the Chemical Index of Alteration as a paleoclimatic indicator: an example from the Permian of the Paraná Basin, Brazil. Palaeogeogr. Palaeoclimatol. Palaeoecol. 293, 175–183.

Gulbranson, E.L., Montañez, I.P., Tabor, N.J., 2011. A proxy for humidity and flora province from paleosols. J. Geol. 119, 559–573.

Harper, D.T., Suarez, M.B., Uglesich, J., You, H., Li, D., Dodson, P., 2021. Aptian-Albian clumped isotopes from Northwest China: cool temperatures, variable atmospheric pCO2 and regional shifts in the hydrologic cycle. Clim. Past 17, 1607–1625.

He, W., He, H., Zhu, M., 2015. Calcium Nodules as a Proxy for Quaternary Paleoclimate Change on China's Loess Plateau. PLoS One 12, e0143928. https://doi.org/10.1371/journal.pone.0143928.

Hyland, E.G., Sheldon, N.D., 2013. Coupled CO2-climate response during the early Eocene Climatic Optimum. Palaeogeogr. Palaeoclimatol. Palaeoecol. 369, 125–135.

Hyland, E.G., Sheldon, N.D., 2016. Examining the spatial consistency of palaeosol proxies: Implications for palaeoclimatic and palaeoenvironmental reconstructions in terrestrial sedimentary basins. Sedimentology 63, 959–971.

Kahmann, J.A., Driese, S.G., 2008. Paleopedology and geochemistry of late Mississippian (Chesterian) Pennington Formation paleosols at Pound Gap, Kentucky, USA: Implications for high-frequency climate variations. Palaeogeogr. Palaeoclimatol. Palaeoecol. 259, 357–381.

Kogler, S.J., Hembree, D.I., 2019. Influences of Modern Pedogenesis on Paleoclimate estimates from Pennsylvanian and Permian Paleosols, Southeastern Ohio, U.S.a. J. Sediment. Res. 89, 227–241.

Komadel, P., 2016. Acid activated clays: Materials in continuous demand. Appl. Clay Sci. 131, 84–99. https://doi.org/10.1016/j.clay.2016.05.001.

Komadel, P., Madejová, J., 2006. Chapter 7.1 Acid Activation of Clay Minerals. In: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), Handbook of Clay Science, Developments in Clay Science. Elsevier, pp. 263–287. https://doi.org/10.1016/S1572-4352(05)01008-1.

Komadel, P., Madejová, J., Janek, M., Gates, W.P., Kirkpatrick, R.J., Stucki, J.W., 1996. Dissolution of Hectorite in Inorganic Acids. Clay Clay Miner. 44, 228–236. https://doi.org/10.1346/CCMN.1996.0440208.

Kraus, M.J., Riggins, S., 2007. Transient drying during the Paleocene-Eocene thermal Maximum (PETM): Analysis of paleosols in the bighorn basin, Wyoming. Palaeogeogr. Palaeoclimatol. Palaeoecol. 245, 444–461.

Kumaravel, V., Sangode, S.J., Siddaiah, N.S., Kumar, R., 2009. Major Element Geochemical Variations in a Miocene-Pliocene Siwalik Paleosol Sequence: Implications to Soil Forming Processes in the Himalayan Foreland Basin. J. Geol. Soc. India 73, 759–772.

Leary, R.J., Quade, J., DeCelles, P.G., Reynolds, A., 2017. Evidence from paleosols for low to moderate elevation of the India-Asia suture zone during mid-Cenozoic time. Geology 45, 399–402.

Li, J., Wen, X.Y., Huang, C.M., 2016. Lower cretaceous paleosols and paleoclimate in Sichuan Basin, China. Cretac. Res. 62, 154–171.

Li, J., Huang, C.-M., Yang, G.-L., Pan, Y.-Y., Wen, X.-Y., 2022. Middle Jurassic climate oscillations from paleosol records of the Sichuan Basin, SW China. J. Palaeogeogr. 11, 97–122. https://doi.org/10.1016/j.jop.2022.01.003.

Lukens, W.E., Lehmann, T., Peppe, D.J., Fox, D.L., Driese, S.G., McNulty, K.P., 2017. The early Miocene critical Zone at Karungu, Western Kenya: an Equatorial, Open Habitat with few Primate remains. Front. Earth Sci. 5.

Lukens, W.E., Nordt, L.C., Stinchcomb, G.E., Driese, S.G., Tubbs, J.D., 2018. Reconstructing pH of Paleosols using Geochemical Proxies. J. Geol. 126, 427–449.

Lukens, W.E., Stinchcomb, G.E., Nordt, L.C., Kahle, D.J., Driese, S.G., Tubbs, J.D., 2019. Recursive Partitioning Improves Paleosol Proxies for Rainfall. Am. J. Sci. 319, 819–845.

Machette, M.N., 1985. Calcic soils of the southwestern United States. In: Weide, D.L., Faber, M.L. (Eds.), Soils and Quaternary Geology of the Southwestern United States. Geological Society of America, pp. 1–21.

Marbut, C.F., 1935. Atlas of American Agriculture. III Soils of the United States. Government Printing Office, Washington D.C.

Maynard, J.B., 1992. Chemistry of modern soils as a guide to interpreting Precambrian paleosols. J. Gelogy 100, 279–289.

Medaris Jr., L.G., Driese, S.G., Stinchcomb, G.E., 2017. The Paleoproterozoic Baraboo paleosol revisited: Quantifying mass fluxes of weathering and metasomatism, chemical climofunctions, and atmospheric pCO2 in a chemically heterogenous protolith. Precambrian Res. 301, 179–194.

Montañez, I.P., Tabor, N.J., Niemeier, D., DiMichele, W.A., Frank, T.D., Fielding, C.R., Isbell, J.L., Birgenheier, L.P., Rygel, M.C., 2007. CO2-Forced climate and Vegetation Instability during late Paleozoic Deglaciation. Science (80-.) 315, 87–91.

Mora, C.I., Driese, S.G., Colarusso, L.A., 1996. Middle to late Paleozoic Atmospheric CO2 Levels from Soil Carbonate and Organic Matter. Science (80-.) 271, 1105–1107.

Mouraviev, F.A., Arefiev, M.P., Silantiev, V.V., Eskin, A.A., Kropotova, T.V., 2020. Paleosols and host rocks from the Middle-Upper Permian reference section of the Kazan Volga region, Russia: a case study. Palaeoworld 29, 405–425.

Myers, T.S., Tabor, N.J., Rosenau, N.A., 2014. Multiproxy approach reveals evidence of highly variable paleoprecipitation in the Upper Jurassic Morrison Formation (western United States). GSA Bull. 126, 1105–1116.

Nesbitt, H.W., Young, G.M., 1982. Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. Nature 290, 715–717.

Nordt, L.C., Driese, S.D., 2010a. New weathering index improves paleorainfall estimates from Vertisols. Geology 38, 407–410.

Nordt, L.C., Driese, S.D., 2010b. A Modern Soil Characterization Approach to Reconstructing Physical and Chemical Properties of Paleo-Vertisols. Am. J. Sci. 310, 37–64. https://doi.org/10.2475/01.2010.02.

Nordt, L., Atchley, S., Dworkin, S., 2015. Collapse of the late Triassic megamonsoon in western equatorial Pangea, present-day American Southwest. GSA Bull. 127, 1798–1815.

Novák, I., Čı́čel, B., 1978. Dissolution of Smectites in Hydrochloric Acid: II. Dissolution Rate as a Function of Crystallochemical Composition. Clay Clay Miner. 26, 341–344. https://doi.org/10.1346/CCMN.1978.0260504.

Osthaus, B., 1955. Kinetic Studies on Montmorillonites and Nontronite by the Acid-Dissolution Technique. Clay Clay Miner. 4, 301–321. https://doi.org/10.1346/CCMN.1955.0040134.

Ostrom, M.E., 1961. Separation of Clay Minerals from Carbonate Rocks by using Acid. J. Sediment. Petrol. 31, 123–129.

Pan, Y., Huang, C., 2014. Quantitative reconstruction of early cretaceous paleoclimate using paleosol carboantes in China. Carbonates Evaporites 29, 327–335.

Pentrák, M., Czímerová, A., Madejová, J., Komadel, P., 2012. Changes in layer charge of clay minerals upon acid treatments as obtained from their interactions with methylene blue. Appl. Clay Sci. 55, 100–107.

Pereira, C.T., Batezelli, A., Ladeira, F.S.B., 2015. Paleoprecipitation changes based on Paleosol Profiles of the Marília Formation (Upper cretaceous) in the Eastern Portion of the Bauru Basin in Southeastern Brazil. Geociências 34, 238–257.

Prochnow, S.J., Nordt, L.C., Atchley, S.C., Hudec, M.R., 2006. Multi-proxy paleosol evidence for middle and late Triassic climate trends in eastern Utah. Palaeogeogr. Palaeoclimatol. Palaeoecol. 232, 53–72.

Ramnarine, R., Voroney, R.P., Wagner-Riddle, C., Dunfield, K.E., 2011. Carbonate removal by acid fumigation for measuring the δ13C of soil organic carbon. Can. J. Soil Sci. 91, 247–250. https://doi.org/10.4141/cjss10066.

Rasmussen, C., Tabor, N.J., 2007. Applying a Quantitative Pedogenic Energy Model across a Range of Environmental Gradients. Soil Sci. Soc. Am. J. 71, 1719–1729.

Retallack, G.J., 1991. Untangling the Effects of Burial Alteration and Ancient Soil Formation. Annu. Rev. Earth Planet. Sci. 19, 183–206.

Rouzaut, S., Campodonco, V.A., Pasquini, A.I., 2021. Weathering and paleoprecipitation indices in a late Pleistocene-Holocene loess-paleosol sequence in Central Argentina. Environ. Earth Sci. 80, 28. https://doi.org/10.1007/s12665-020-09324-5.

Royer, D.L., Berner, R.A., Montañez, I.P., Tabor, N.J., Beerling, D.J., 2004. CO2 as a primary driver of Phanerozoic climate. GSA Today 14, 4–10.

Sheldon, N.D., 2003. Pedogenesis and geochemical alteration of the Picture Gorge subgroup, Columbia River basalt, Oregon. GSA Bull. 115, 1377–1387.

Sheldon, N.D., Tabor, N.J., 2009. Quantitative paleoenvironmental and paleoclimatic reconstruction using paleosols. Earth-Science Rev. 95, 1–52.

Sheldon, N.D., 2006. Quaternary glacial-interglacial climate cycles in Hawaii. J. Geol. 114, 367–376.

Sheldon, N.D., Retallack, G.J., Tanaka, S., 2002. Geochemical Climofunctions from north American Soils and Application to Paleosols across the Eocene-Oligocene Boundary in Oregon. J. Geol. 110, 687–696.

Soil Survey Staff, 2010. Keys to Soil Taxonomy, 11th ed. USDA-Natural Resources Conservation Service, Washington, D.C.

Southard, R.J., Driese, S.G., Nordt, L.C., 2012. Vertisols. In: Huang, P.M., Li, Y., Sumner, M.E. (Eds.), Handbook of Soil Science. CRC Press, Boca Raton, Florida, pp. 33–97.

Srivastava, P., Patel, S., Singh, N., Jamir, T., Kumar, N., Aruche, M., Patel, R.C., 2013. Early Oligocene paleosols of the Dagshai Formation, India: a record of the oldest tropical weathering in the Himalayan foreland. Sediment. Geol. 294, 142–156.

Stinchcomb, G.E., Nordt, L.C., Driese, S.G., Lukens, W.E., Williamson, F.C., Tubbs, J.D., 2016. A data-driven spline model designed to predict paleoclimate using paleosol geochemistry. Am. J. Sci. 316, 746–777.

Thomas, S.G., Tabor, N.J., Yang, W., Myers, T.S., Yang, Y., Wang, D., 2011. Palaeosol stratigraphy across the Permian-Triassic boundary, Bogda Mountains, NW China: Implications for palaeoenvironmental transition through earth's largest mass extincton. Palaeogeogr. Palaeoclimatol. Palaeoecol. 308, 41–64.

Varela, A.N., Raigemborn, M.S., Richiano, S., White, T., Poiré, D.G., Lizzoli, S., 2017. Late cretaceous paleosols as paleoclimate proxies of high-latitude Southern Hemisphere: Mata Amarilla Formation, Patagonia, Argentina. Sediment. Geol. 363, 83–95.

Wilding, L.P., Tessier, D., 1988. Genesis of Vertisols: Shrink-swell phenomena. In: Wilding, L.P., Puentes, R. (Eds.), Vertisols: Their Distribution, Properties, Classification and Management. Texas A&M University Printing Center, College Station, TX, pp. 1–22.

Yapp, C.J., Poths, H., 1992. Ancient atmospheric CO2 pressures inferred from natural goethites. Nature 355, 342–344.